

GPO PRICE \$ _____

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Hard copy (HC) 3.00

Microfiche (MF) 50

ff 653 July 65

Report No. IITRI-C6014-26
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS

George C. Marshall Space Flight Center
National Aeronautics & Space Administration
Huntsville, Alabama

N65-35112

(ACCESSION NUMBER)

(THRU)

59
(PAGES)

1
(CODE)

CK 67250
(NASA CR OR TMX OR AD NUMBER)

17
(CATEGORY)

FACILITY FORM 505

Report No. IITRI-C6014-26
(Triannual Report)

DEVELOPMENT OF SPACE-STAPLE THERMAL-CONTROL COATINGS

Contract No. NAS8-5379
IITRI Project C6014

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July 1965

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FOREWORD

This is Report No. IITRI-C6014-26 (Triannual Report) of IITRI Project C6014, Contract No. NAS8-5379, entitled "Investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles." The report covers the period from January 20 through May 20, 1965. Previous Triannual Reports were issued on October 25, 1963, March 5, 1964, July 20, 1964, December 21, 1964, and February 23, 1965.

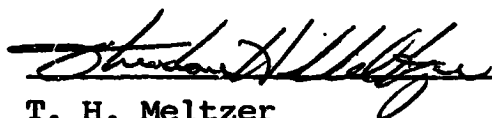
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Data are recorded in IITRI Logbooks C13423, C13736, C13802, and C14176.

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ABSTRACT

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

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This report describes studies aimed at the development of stable thermal-control coatings with the lowest possible ratio of solar absorptance to infrared emittance.

The studies of inorganic pigments involved the screening of several potassium silicate paints pigmented with zinc titanate, zirconia, hafnia-free zirconia, zirconium spinel, and several rare earth oxides (yttrium, lanthanum, and tantalum oxides).

The studies of methyl silicone paint confirmed the excellent stability of zinc oxide paints based upon Owens-Illinois type 650 glass resins. Photolysis experiments were carried out on specially prepared methyl silicone polymers by using mass spectroscopy and electron spin resonance techniques. Some differential spectroscopy measurements were performed to provide a basis for eventual correlation of absorption-band development with type of defect and defect location.

author

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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

I. INTRODUCTION

The general requirement under this contract is for thermal-control surface coatings with a very low but stable ratio of solar absorptance (α) to infrared emittance (ϵ). The work is currently proceeding in two major directions: (1) studies of inorganic pigments and (2) studies of methyl silicone photolysis. Secondary efforts involve (1) synthesis of methyl silicone polymers in support of the photolysis investigations, (2) investigations of inorganic pigment binders, and (3) general screening of zinc oxide-pigmented silicones and potentially useful polymers.

The studies of inorganic pigments involve screening and evaluation of materials parameters that affect pigment stability. These studies are aimed at finding or preparing stable pigments that are potentially useful in formulating coatings with a very low solar absorptance.

The studies of methyl silicone photolysis involve electron spin resonance and mass spectrometry investigations of carefully prepared methyl and methyl-aromatic silicones irradiated with ultraviolet in a vacuum at the following temperatures: liquid nitrogen, ambient (60°C), and elevated (150°C). These studies are aimed at explaining the mechanism of ultraviolet degradation of methyl silicone polymers and will, we hope, lead to the

synthesis of more stable systems.

The polymer synthesis work is oriented almost exclusively toward preparing photolysis-resistant materials and involves the synthesis of linear polydimethylsiloxanes, oxidatively cross-linked polymethylsiloxanes, and polymethyl(phenyl)siloxanes with carefully controlled methyl-to-phenyl ratios.

Because zinc oxide-pigmented coatings have exhibited the best stability to ultraviolet irradiation in vacuum, zinc oxide is being used in the screening program to pigment potentially useful polymers that are received from time to time from industry and NASA. This screening program has resulted in establishing the exceptional stability of Owens-Illinois type 650 methyl silicone "Glass Resins".

II. INORGANIC COATINGS

A. Introduction

Current studies of inorganic coatings can be divided into two general categories: screening studies and studies of the material parameters affecting degradation.

Screening tests are generally confined to dielectric pigments, that is, those materials that have a band gap greater than about 6 eV and that do not absorb near ultraviolet radiation. Semiconductor pigments, such as zinc oxide, which has a band gap of 3.3 eV, characteristically absorbs radiation beginning at 3800 Å and generally cannot be utilized in very low-solar-absorptance coatings because their absorptance is too high even when they do not degrade. Screening tests are conducted with pigment samples to eliminate binder effects. Promising pigments are then made into coatings for further evaluation.

The probability seems increasingly remote that screening tests will uncover a pigment that is whiter than zinc oxide and equal to it in resistance to degradation. While these tests will be continued, emphasis will be placed on improving the properties of known pigments that are whiter (i.e., have a higher refractive index and higher ultraviolet reflectance) than zinc oxide but more degradable. Dielectric materials such as zirconia, alumina, and magnesia will be studied to determine the effect of variation of material parameters on

degradation. The surface area, absorbed gases, particle size, method of preparation, etc. will be varied and the effects noted. Zinc titanate will also be studied, since previous work suggests that it may be possible to develop a pigment that has greater whiteness than zinc oxide alone and has only slightly inferior degradation resistance.

B. Results

During this report period several coating systems using non-zinc oxide pigments in potassium silicate binder were examined optically and subjected to an ultraviolet-vacuum environment. Included in these studies were zinc titanate samples supplied by New Jersey Zinc Company, zirconia samples including hafnia-free zirconia supplied by Wah Chang Corporation, "zirconium spinel" supplied by TAM, and a variety of other materials. Four screening tests were completed, No. V59, V61, and V63, and the results are given in Table 1. Other tests are presently under way.

Among the zinc titanate coatings, A-54-1 had the highest stability. As noted in previous reports, A-54-2 contains both unreacted zinc oxide and titania, whereas 602-26-1M zinc titanate contains no excesses. In an effort to improve its stability, A-54-2 was heated in air for 16 hr at 700°C. This resulted in an improved (lower) solar absorptance (α) but a great increase in change in absorptance ($\Delta\alpha$). This is the second instance in which heat treatment did not improve

Table 1

EFFECT OF UV IRRADIATION IN VACUUM ON VARIOUS SILICATE-BONDED COATINGS AND PIGMENTS

Test	Sample No.	Pigment	PBR ^a	Exposure, ESH	Solar Absorptance			
					α_1	α_2	α_a	γ_a
V59	7045	602-26-1M ZnTiO ₃ (700°C/4 hr)	4.30	0 750	.067 .098	.071 .071	.138 .169	- .031
V59	7047	A-54-2 ZnTiO ₃ (700°C/16 hr)	4.30	0 750	.056 .073	.061 .065	.117 .138	- .021
V62	7105	A-54-2 ZnTiO ₃ (700°C/16 hr)	5.38	0 0, heated ^d 330	.039 .032 .048	.024 .016 .025	.063 .047 .073	- -.016 .026
V62	7106	A-54-2 ZnTiO ₃ (700°C/16 hr)	5.38	0 330	.039 .044	.027 .027	.066 .071	- .005
V59	7049	C.P. ZrO ₂ (300°C/4 hr)	4.30	0 750	.072 .144	.119 .129	.191 .273	- .082
V59	7050	C.P. ZrO ₂ (300°C/4 hr)	6.45	0 750	.049 .097	.074 .076	.123 .173	- .050
V61	7094	C.P. ZrO ₂ (300°C/4 hr)	6.45	0 2090	.041 .103	.034 .038	.075 .140	- .065
V61	7095	C.P. ZrO ₂ (300°C/4 hr)	6.45	0 0, heated ^d 2090	.039 .128 .153	.039 .095 .097	.078 .223 .250	- -.145 .027
V61	7097	C.P. ZrO ₂ (300°C/4 hr)	4.30	0 2090	.063 .115	.090 .096	.152 .211	- .059
V62	7111	C.P. ZrO ₂ (300°C/4 hr)	4.30	0 330	.061 .087	.094 .096	.155 .183	- .028
V63	7145	C.P. ZrO ₂	6.45	0 2000	.047 .134	.060 .053	.107 .187	- 0.080
V63	7146	Hafnia-free ZrO ₂	6.45	0 2000	.061 .166	.056 .056	.117 .222	- 0.105
V55	7051	SP 500 ZnO (600°C/16 hr)	4.30	0 750	.083 .091	.069 .067	.152 .158	- .006
V61	7092	"Zirconium Spinel" (1700°C/16 hr)	4.30	0 2090	.058 .141	.047 .050	.104 .193	- .089
V61	7093	"Zirconium Spinel" (1000°C/16 hr)	4.30	0 0, heated ^d 2090	.049 .043 .115	.047 .034 .042	.096 .076 .157	- -.020 .081
V62	7101	Y ₂ O ₃	4.30	0 0, heated ^d 330	.037 .028 .084	.055 .044 .048	.087 .072 .132	- -.015 .060
V62	7102	Y ₂ O ₃	4.30	0 330	.034 .126	.050 .050	.084 .177	- .093
V62	7103	La ₂ O ₃	4.30	0 0, heated ^d 330	.016 .035 .090	.053 .056 .053	.068 .091 .142	- .023 .051
V62	7104	La ₂ O ₃	4.30	0 330	.021 .157	.051 .052	.072 .210	- .136
V62	7107	Ta ₂ O ₅ (600°C/2 hr)	4.30	0 0, heated ^d 330	.083 .070 .082	.085 .060 .055	.169 .131 .137	- -.038 .006
V62	7108	Ta ₂ O ₅ (800°C/2 hr)	4.40	0 330	.085 .149	.089 .092	.174 .241	- .067
V62	7109	LiF	No binder	0 330	.017 .050	.024 .027	.041 .078	- .037
V62	7100	LiF	4.30	0 330	.039 .144	.061 .062	.099 .206	- .107
V63	7127	TiO ₂ capacified porcelain enamel	0	0 2000	.116 .121	.212 .204	.328 .325	- -.003

^aPigment-to-binder ratio (PBR) by weight. The binder was PS-7 potassium silicate, cured by drying in air.^bEquivalent-sun-hours (ESH) of exposure to simulated solar radiation. The solar factor was 10X.^cThe binder was glass.^dHeated at 500°C for 2 hr.

resistance to degradation; the first was magnesium aluminate spinel. The reason for this effect is not known; but it may be due to the formation of a titanate that is less stable than ZnTiO_3 , which has a ZnO -to- TiO_2 ratio of 1:1. The formula for these pigments as given by the manufacturer is ZnTiO_3 . A number of compounds are formed in the ZnO - TiO_2 system. Bartram and Slepety's (ref. 1) identify three compounds, while Loskarev (ref. 2) identifies six, with ZnO - TiO_2 ratios varying from 1:2 to 3:1. An x-ray analysis is being made to determine which compounds are present in these pigments, and an attempt will be made to obtain all the compounds formed in this system and test them.

The effect of varying the pigment-to-binder ratio (PBR) of coatings with zirconia pigments was studied, and contradictory results were obtained. In Test V59, increasing the PBR from 4.30 to 6.45 improved stability as well as significantly lowered solar absorptance. The former effect is somewhat paradoxical in view of previous experiments that showed the pure pigment to be much less stable than a silicate system incorporating the pigment. A repeat experiment, Test V61, yielded results more in line with past experience, the high-PBR sample being somewhat less stable than the low-PBR one. The effect of heat treatment was also studied on zirconia-pigmented coatings. A coating with a PBR of 4.30 was tested previously and showed an increase in solar absorptance after heat treatment. The increase was much more pronounced for a coating with a PBR of 6.45 in Test V61.

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Hafnium is closely similar in its properties to zirconium and is found in nearly all zirconium ores. The average concentration is 2 to 3%, but deposits with concentrations up to 22% have been discovered. The extraction of hafnium from zirconium is difficult. As a consequence, all commercial zirconias for ceramic applications, including the CP (chemically pure) zirconia used as a pigment, contain 2 to 3% hafnia. However, for atomic energy applications, hafnia-free zirconia is required, and zirconia with less than 0.1% hafnia is now available commercially. Some of this material was obtained and compared with the standard CP zirconia. The hafnia-free material was inferior to the CP grade in both initial solar absorptance and change in absorptance, indicating that the presence of hafnia has no adverse effect.

Zirconium spinel, an opacifying agent marketed by the Titanium Alloys Division of the National Lead Corporation, had shown fair stability in a previous test, V58. However, the present test, V61, showed this material to be an unsuitable pigment as evidenced by solar absorptance changes in excess of 0.08. The positive value of heat treatment for lowering the initial solar absorptance and also for improving stability is manifest in the results of this experiment.

Coatings pigmented with a variety of materials hitherto unstudied were examined in Test V62. With the exception of a fired tantalum oxide coating, all the new coatings degraded appreciable in this short test (330 ESH). Firing the tantalum oxide resulted in improved initial reflectance, as well as

excellent stability.

The lithium fluoride pigment sample had a much lower solar absorptance and solar absorptance change than the silicate-bonded coating. Neither pigment nor coating showed any sharp absorptance at 4000 Å, the F-center color band for lithium fluoride.

A sample of titania-opacified porcelain enamel, obtained from Chicago Vitreous Corporation, was included in the last test, V63. The initial solar absorptance was 0.328, while the final solar absorptance was 0.325. The slight degradation in the ultraviolet and the visible regions ($\Delta\alpha_1$ of - 0.005) was more than offset by bleaching in the infrared region ($\Delta\alpha_2$ of + 0.008). This is surprising, since titania is normally not a stable pigment under the test conditions. It has been suggested that the presence of hydroxyl ions is essential to develop color in white oxides exposed to ultraviolet radiation and that the pigments used in these coatings can absorb appreciable amounts of water, which is retained even when the coating is calcined (ref. 3,4). For example, titania heated to 505°C had a water content of 1.4 mg/g (ref. 5). The incorporation of this material into a vitreous enamel may have rendered it completely anhydrous and prevented water from being absorbed when the coating was cool. Another possibility is that the glassy matrix prevented appreciable oxygen diffusion, so that any oxygen liberated by ultraviolet irradiation recombined immediately. This is an interesting result and deserves further study.

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C. Future Work

A number of materials are on hand for screening tests, and others are being procured.

It has been noted in past tests that the stability of a pigment increases with increasing particle size or decreasing surface area; indeed, this may be the primary effect of heat treatment. Therefore, zinc oxide with an average particle size of 1.2μ prepared from SF 500 has been obtained from the New Jersey Zinc Company and will be compared with standard SP 500 pigment.

It is known that the Fermi level of zinc oxide can be lowered by substitutional doping with lithium, and it has been suggested that, while the overall reflectance might be lowered slightly by doping, subsequent ultraviolet-induced degradation might be reduced or completely eliminated (ref. 6). Therefore, samples of USP-12 (a pure pharmaceutical grade of zinc oxide) that have been doped with 0.01 and 0.1 mol % of Li have been obtained from New Jersey Zinc Company and will be compared with undoped USP-12.

Therefore, extremely pure alumina (less than 100 ppm of impurities) prepared at IITRI some years ago (ref. 7 and 8) will be studied. Also, Professor Ivan Cutler of the University of Utah (ref. 9) has indicated that he will be able to supply samples of alumina and magnesia of high purity and doped with various oxides.

A study of very pure materials may suggest possible means

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to improve degradation resistance of very white compounds.

The decrease in stability shown by hafnia-free zirconia when compared with standard CP zirconia containing 2 to 3% hafnia suggests that hafnia may be a superior pigment to zirconia. An approximate calculation using the Lorenz-Lorentz equation plus its place in the same column of the periodic table as zirconium and titanium indicate that hafnia's index of refraction will be of the same order, although no data could be found in the literature. A sample will be obtained for evaluation.

Zirconia and zinc titanate have been selected as two materials to be studied in detail in an attempt to determine the preparation variables that affect reflectance and degradation. Zirconia was selected as one model material because (1) it has high index of refraction (2.19 versus 2.00 for zinc oxide) and a low solar absorptance, (2) it exists in three different crystalline phases, which can be considered as distortions of a cubic lattice with different lattice energies, (3) it is an intrinsic insulator but forms solid solutions with various oxides, thus changing the crystal structure and semiconductor properties, and (4) it can be prepared from several compounds that are available in high purity. The zinc oxide/titanium oxide system was selected because past work indicates that it might be possible to develop a pigment whiter than zinc oxide alone and similar in degradation resistance.

The initial experiments with zirconia will include varying the starting materials (zirconium oxychloride and sulfate are

on hand in both CP and hafnia-free grades), varying the calcining atmosphere (O_2 , H_2 , A, and vacuum), and varying the calcining temperature (500, 750, 1000, 1250°C). The exposure to simulated solar radiation will be done in both a hard vacuum and in air. The results of these experiments may suggest answers to such hypotheses as: degradation of materials is caused by oxygen deficiency, the surface layer of powders is significantly different from their bulk properties and controls degradation, and absorbed surface layers of gases have a significant effect on the photolysis of fine powders.

Experiments with the zinc oxide/titanium oxide system will be limited to obtaining or preparing the various chemical compounds that exist and determining their reflectance and resistance to degradation. If these efforts show promise, a more extensive study will be made.

The materials used in these coatings are very fine powders, and many of these materials are known to have high surface activity that is dependent on their past history. For example, the free energy of zinc oxide has been shown to be dependent on the method of preparation (ref. 10). It is essential that these materials be studied as fine powders despite the difficulties involved, since in some instances the bulk properties of a material are greatly changed by minute subdivision. For example, fused silica windows do not degrade when exposed to prolonged ultraviolet irradiation, but powdered silica degrades severely, an effect that could not be predicted from examination of the bulk material.

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III. METHYL SILICONE PAINTS

Test V63 included a number of methyl silicone coatings. The results are shown in Table 2.

The zinc oxide-pigmented coatings utilizing Owens-Illinois type 650, lot 1040 resin again showed outstanding ultraviolet stability. Because of the previous experience with the Glass Resin coatings, we used type 650 resin as the vehicle for examining the stability of the titanium dioxide obtained from Cabot Corporation ("Flame-Process" rutile). Sample 5130 exhibited the lowest increase in solar absorptance of any rutile-pigmented organic coating examined to date.

Sample 5128, IITRI's S-13 paint, was cured with the proprietary Shell H-2 catalyst rather than the SRC-05 catalyst specified by General Electric. The degradation exhibited is not consistent with the improvement in stability previously achieved with the Shell H-2 catalyst. We suspect, that the concentration of catalyst, whether H-2 or SRC-05, is the more important parameter in determining the resultant stability of the S-13 system.

Eight S-13 specimens are not listed in Table 2. These specimens were developed under Contract NAS8-11136, IITRI Project C6025, for the Pegasus A and B spacecraft. They exhibited average absorptance increases of 0.017 after 2000 ESH in test V63.

Table 2

EFFECT OF UV IRRADIATION IN VACUUM ON METHYL SILICONE PAINTS
(TEST V63)

Sample No.	Vehicle	PVC ^a	Pigment	Exposure, ESH,	Solar Absorptance		
					α_1	α_2	$\Delta\alpha$
5126	Owens-Illinois type 650 glass resin, lot 1040	30%	SP500 ZnO	0 2000	.098 .100	.101 .097	.199 .197 +.002
5127	Owens-Illinois type 650 glass resin, lot 1040	30%	SP500 ZnO	0 2000	.100 .102	.104 .096	.204 .198 -.006
5128	LTV-602 + Shell H-2	30%	SP500 ZnO	0 2000	.097 .128	.099 .097	.196 .225 +.029
5130	Owens-Illinois type 650 glass resin, lot 1040	35%	Cabot's flame-process rutile	0 2000	.103 .113	.102 .117	.205 .230 +.025

^aPigment volume concentration.

IV. METHYL SILICONE PHOTOLYSIS

A. Introduction

The ultimate objective of this portion of the program is the synthesis of silicone polymers that are totally resistant to solar radiation. The immediate objectives are (1) to determine the inherent stability of the basic silicone structure, (2) to determine the mechanism of ultraviolet-degradation processes, (3) to assess the influence of various side chain or substituent groups, and (4) to assess the influence of contamination on the photolytic processes and to identify those contaminants which promote or otherwise affect polymer degradation.

Ultraviolet photolysis of the silicone polymers is being followed by (1) ultraviolet (differential) absorption spectroscopy, (2) mass spectrometry and (3) electron spin resonance spectroscopy.

B. Ultraviolet Absorption Spectroscopy

Ultraviolet absorption spectroscopy provides the chemist with a useful tool for determining the behavior of materials to both ionizing and ultraviolet irradiation. Its usefulness, however, depends to a great extent upon the techniques employed in obtaining spectra. That is, the peak wavelength (absorption-band maxima) assignments depend not only on the resolution of the instruments employed but also on the purity of the materials and such influencing factors as, for example, solvent effects, which are known to considerably displace maxima. Furthermore, additional

errors occur in differential spectra obtained by the subtraction of one transmittance spectrum from another.

The data obtained thus far were aimed at determining the influence of the solvent used to prepare the silicone films and to elucidate the general character of the ultraviolet-induced absorption bands formed in variously cured methyl silicone films. Therefore, while the information usually plotted is molar absorptivity, ϵ , versus frequency, ν , we obtained the curves as transmittance, T , versus wavelength, λ . Careful analysis requires that the abscissa be plotted as frequency in order to obtain the symmetry needed for band separation. Furthermore, half-widths are, by definition, the band width in wave numbers at $\epsilon_{\text{max}}/2$. We have, for the purpose of communication, indicated the band half-widths as the band width in angstroms at $T_{\text{max}}/2$.

A number of clear films of RTV-602 methyl silicone polymer (used in S-13 paints) plus three other methyl silicone films were irradiated for 750 ESH in Tests V57 and V59. Differential absorption spectra were computed from spectral transmittance spectra obtained before and after irradiation. The absorption-band assignments for the various films are given in Table 3. Typical spectra are shown in Figures 1 and 2. Double absorption bands were observed for the RTV-602 films cured with amines; Figure 1 shows the effect of ultraviolet in vacuum on an RTV-602 film cured with diethanolamine. The RTV-602 cured with tin octoate and the experimental methyl silicone resin, R-9, cured with tetrabutoxy titanium showed only one absorption band (Figure 2).

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Table 3

ABSORPTION BANDS^a FORMED DURING UV IRRADIATION OF SILICONE FILMS FOR 750 ESH

Sample No.	Polymer	Cure or Additive	Substrate	Absorption-Band Peak		Remarks ^b
				Wavelength, A	Intensity, % T	
5031	LTV-602	Diethanolamine	Suprasil	2400 2800	68 67	medium; HW = 400 A broad, long tail; HW = 1600 A
5032	LTV-602	Diethanolamine plus toluene	Suprasil	2400 2750	71 69	medium; HW = 400 A broad, long tail; HW = 1600 A
5015	LTV-602	Tin octoate	Free film	3230	38	broad, long tail; HW = 1000 A
5018	LTV-602	Tin octoate plus toluene	Reflectance (on aluminum)	2890	33	broad, long tail; HW = 550 A
5029	LTV-602	Ethylenediamine	Suprasil	2400 2750	26 26	medium; HW = 300 A broad, long tail; HW = 900 A
5030	LTV-602	Ethylenediamine plus toluene	Suprasil	2400 2800	35 33	medium; HW = 380 A broad, long tail; HW = 1000 A
5017	LTV-602	Diethylamine	Reflectance (on aluminum)	2430 2950	11 18	medium; HW = 240 A broad, long tail; HW = 1550 A
5027	LTV-602	Shell H-2	Suprasil	2300 2800	30 9	medium; HW = 350 A HW not discernible
5028	LTV-602	Shell H-2 plus toluene	Suprasil	2370 2800	16 15	medium; HW = 220 A broad, long tail HW = 620A
5033	OI 650 (lot 1004)	300°F for 1 hr	Suprasil	2260 2800	6 7	broad; HW = 230 A broad; HW = 600 A
5034	Exptl. R-9	Tetrabutoxy titanium (TBT)	Suprasil	2480	45	medium; HW = 300 A
5035	Q92-009	Room Temp.	Suprasil	2450 2760	72 75	medium; HW = 550 A broad, long tail; HW = 1260 A

^aAll bands determined by transmittance measurements except as noted.^bHalf-band widths are approximate.

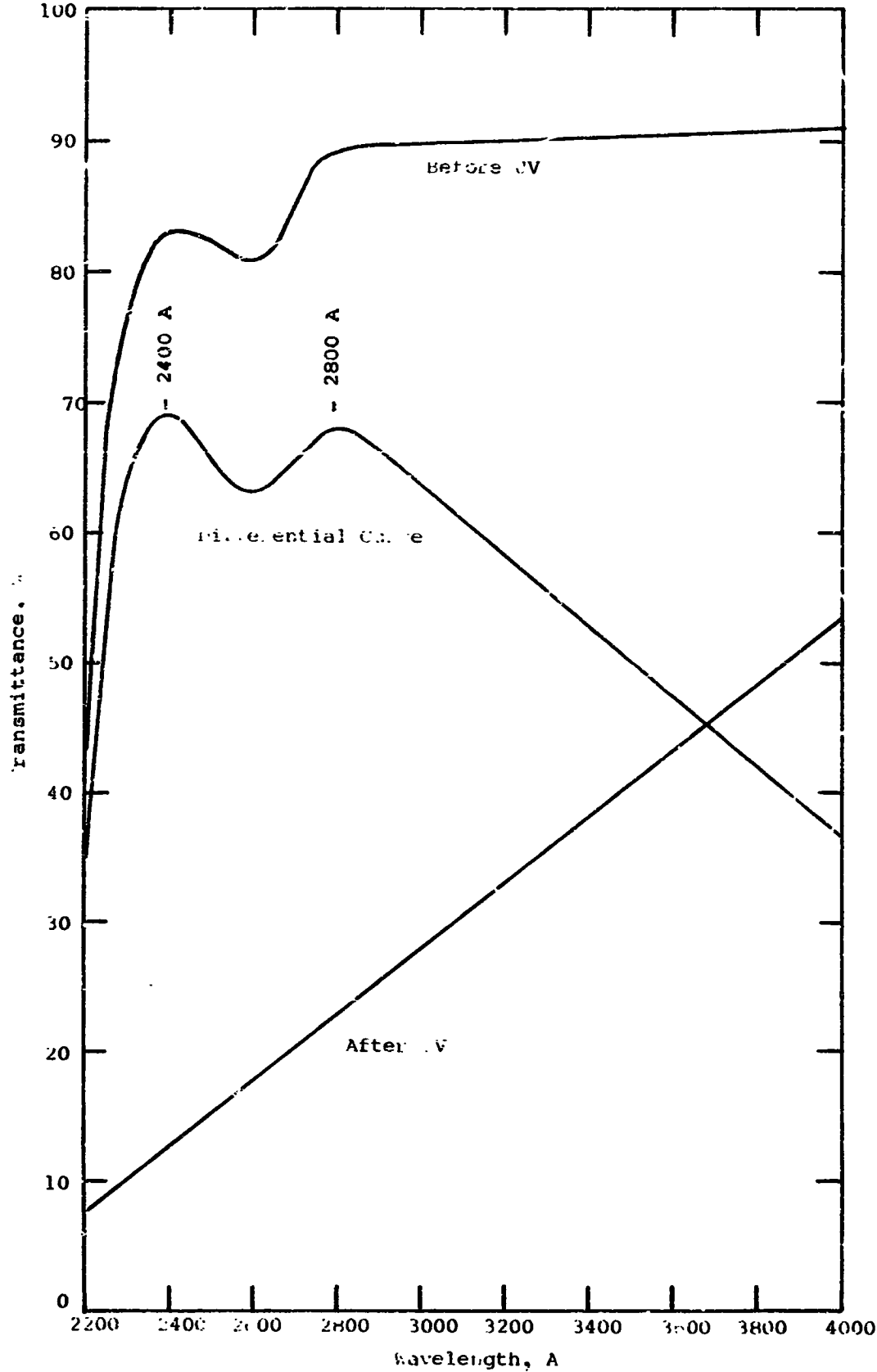
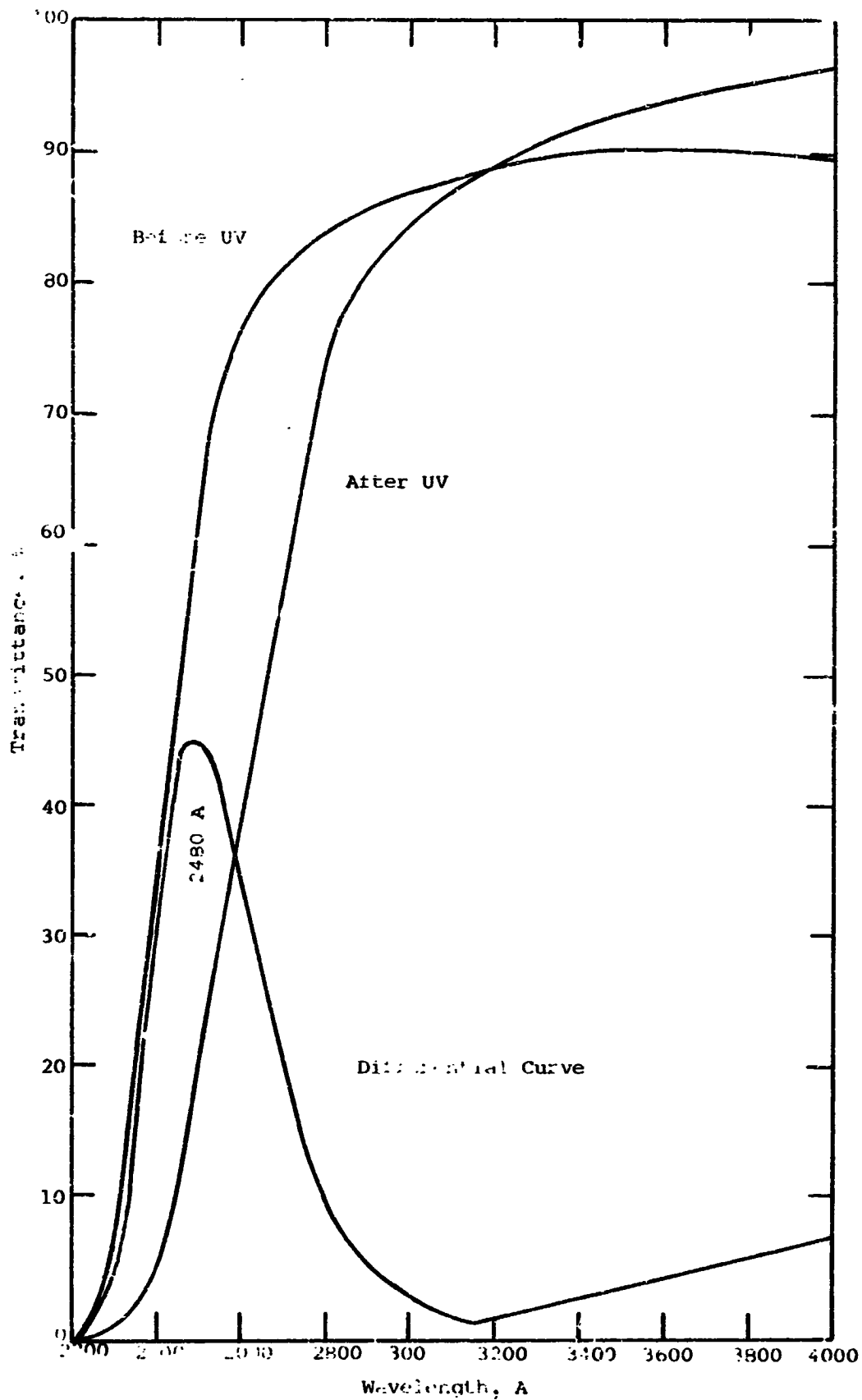


Figure 1

DIFFERENTIAL, UV TRANSMITTANCE SPECTRA
OF RTV-602 CURED WITH DIETHANOLAMINE



DIFFERENTIAL UV TRANSMITTANCE SPECTRA
OF EXPERIMENTAL RESIN R-9 CURED WITH TETRABUTOXY TITANIUM

The difference between the band peaks for samples 5015 and 5018 (with and without toluene) cannot be explained at this time (Table 3).

The fact that little difference was noted in band assignments for samples 5031 and 5032 (with and without toluene) indicates that any toluene not removed by vacuum soaking did not markedly affect the stability of the RTV-602 films. This is in contrast to previous results obtained with S-13 paints. An increase in intensity of the 2800-A band was noted for the Shell H-2-cured RTV-602 containing toluene, however.

The peak assignments were more arbitrary than desirable since the bands were computed by subtracting one curve from the other, point by point. This problem will be alleviated in future experiments by use of differential spectroscopy techniques.

The dual peaks are thought to represent multiple defects (two major defects) for amine-cured resins in contrast to the essentially single major defect indicated for RTV-602 cured with tin octoate and the similar experimental R-9 resin cured with tetrabutoxy titanium.

The data in Table 3 are still being evaluated and verified by further experimentation. These spectroscopic techniques, along with mass and electron spin resonance spectra will provide valuable information and will help to elucidate the polymer photolysis mechanisms.

C. Photolysis Experiments

1. Equipment

The photolysis investigation is being conducted in the equipment shown in Figure 3. The glass vacuum manifold is pumped by a mercury diffusion pump through two liquid nitrogen traps, producing a net pumping speed of approximately 1 liter/sec for noncondensable species. Pressures in the range of low to mid 10^{-7} torr are ordinarily produced in the empty system after a mild bake out at 150°C . Pressures in the range 10^{-3} to 10^{-7} torr are measured with a hot filament ionization gage. The residual gases in the manifold are analyzed with a 60-degree-sector field Nier-type mass spectrometer (Vacuum Electronics Corp., model GA-4). This instrument has an ultimate sensitivity for nitrogen of 10^{-13} torr and a working sensitivity in these experiments below 10^{-10} torr. The mass range is 2 to 300 AMU.

The polymers are contained in 4-mm OD fused silica tubes and are irradiated with an AH-6 lamp through a quartz envelope of approximately 1-mm thickness at a distance of 4 cm measured from the lamp centerline to the polymer tube centerline, with about 3 cm of the intervening distance filled with liquid nitrogen.

2. Procedures

The polymer is irradiated by attaching the fused silica polymer tube onto the glass manifold with graded seals. A vacuum below 10^{-6} torr is obtained, and liquid nitrogen is slowly admitted to the Dewar surrounding the sample tube. The

--- Mass Spectrometer Tube

Ionization Pressure Gage

--- Pinch -Off
Constriction

Vacuum Manifold

Variable
Leak

Ultraviolet
Lamp

Quartz

Magnetically
Operated
Ball
Valve

Thermocouple
Pressure
Gage

Mechanical
Vacuum
Pump

Liquid Nitrogen
Trap

Double
Liquid
Nitrogen
Traps

Polymer In
Fused Silica
Tubes

Liquid
Nitrogen

Water-Cooled Baffle

Mercury Diffusion
Pump

Figure 3 - Glass Vacuum System For Polymer Irradiation Studies

liquid nitrogen is replenished automatically by a controller, which maintains the liquid level approximately 2 cm from a preset level. After condensation of water from the atmosphere on the inside of the quartz tube was noted in preliminary tests, subsequent tests were conducted with a continuous gaseous nitrogen purge of the lamp cavity.

The polymer is irradiated for a predetermined time and the unshunted polymer tube is then removed, still under a typical vacuum and at liquid nitrogen temperature, for electron spin resonance measurements. The shunted polymer tube is warmed to room temperature, and the evolving gases are analyzed with the mass spectrometer. The first polymer test resulted in great quantities of gas being liberated after warming the polymer from liquid nitrogen temperature. Subsequent testing was accomplished with a variable leak fitted to the system, as shown in Figure 3. After irradiation, the left polymer tube is sealed from the vacuum manifold at the constriction, and the evolving gases are bled into the manifold with the variable leak at a rate sufficiently slow that accurate mass spectrometric analyses can be made.

Mass spectrometer analyses of the residual gases are made on the empty system before the polymer tubes are attached, on the system with the polymer tubes attached and at room temperature, after cooling to liquid nitrogen temperatures, during irradiation, after irradiation while the polymer is still cold, while the evolved gas from the room temperature sample is being bled into

the system, and again with the empty system after the polymer tubes are removed.

3. Test Description

To date, three irradiations have been conducted: two on a linear (liquid) polydimethylsiloxane and one on a solid, oxidatively cross-linked polydimethylsiloxane. The synthesis procedures for these two materials are given in Appendix A. The test parameters and general results are presented in Table 4.

Table 4
EFFECT OF UV IRRADIATION ON SILOXANES

<u>Test</u>	<u>Polymer</u>	<u>Exposure, hr</u>	<u>Remarks</u>
LP-1	Linear	2	Gelation
LP-2	Linear	5	No gelation
SP-1	Cross-linked	5	No color

4. Electron Spin Resonance Spectra

A description of electron spin resonance and its utility is presented in Appendix B.

No electron spin resonance spectra were obtained of the irradiated linear polymers. Figure 4 presents the electron spin resonance spectrum of the irradiated, solid, cross-linked polymer.

The results show the presence of one central strong line

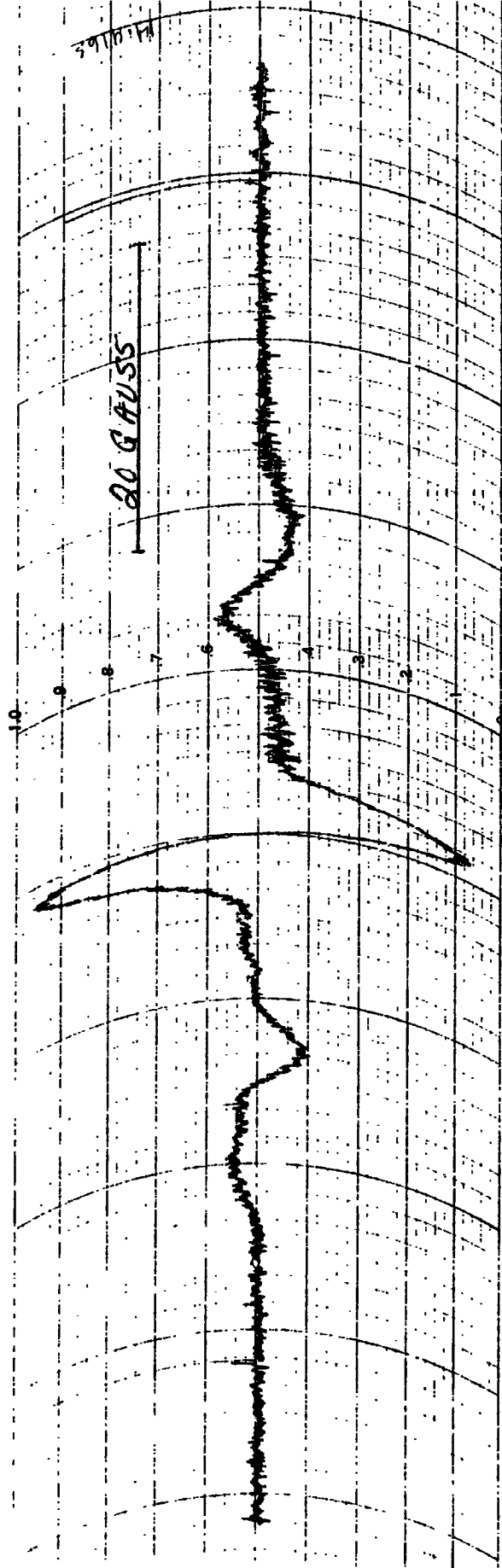
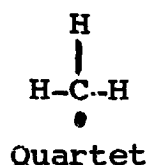
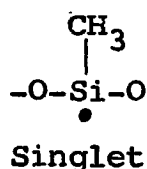


Figure 4

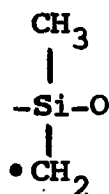
ELECTRON SPIN RESONANCE SPECTRUM
OF IRRADIATED, SOLID, CROSS-LINKED POLYDIMETHYLSILOXANE

and groups of weaker lines. The center line has a g value of 2.0026 which is very close to the free spin value of 2.0023. The subsidiary lines could be hyperfine lines associated with the main line, but this is unlikely in view of the fact that the weaker lines appear to be broader than the main line. Rather, it seems that the weaker lines are due to a separate paramagnetic species associated with a center having a nuclear spin I of 1/2. There are some structures associated with these weaker lines, suggesting that a further set of weaker lines exists. The data are consistent with this third center being associated with two nuclei, each of spin 1/2, although the resolution of the spectrum is not high enough to allow this to be stated unequivocally.

Ormerod and Charlesby (ref. 11) also detect similar spectra and suggest that the singlet and quartet species are:



Tsvetkov et.al., (ref. 12) suggests that the triplet is:



In the present case the data are slightly different from these reported by Cammerod and Charlesby. Specifically, the separation in the doublets is 34 gauss compared to 40 gauss. However, this value may fall within their experimental error.

5. Mass Spectrometry of the Liquid Polymer

In initial attempts to test the liquid polymer, the polymer tubes shattered upon cooling to liquid nitrogen temperature. This resulted in the generation of a considerable number of mass spectrometer scans of background gases and of the gases evolved from the polymer before the shattering occurred. Two subsequent irradiations were accomplished with samples of the liquid polymer, and data were obtained of gases evolved during irradiation and at liquid nitrogen temperatures after irradiation. However, upon warming the first polymer sample, sufficient gas was evolved to preclude mass spectrometric analysis. Because one tube shattered during the cooling of the second sample, it was necessary to analyze the evolved gas from the tube on which the ESR data were taken. Experimental difficulties in accomplishing this made the validity of the data questionable.

Table 5 shows the peak heights of various background gases and gases evolved from the liquid polymer before cooling. The first two columns of data were taken in the test (numbered LP-0) in which the polymer tubes shattered. The next six columns are from the two tests in which irradiation was accomplished (LP-1 and LP-2). The hydrogen peak (2 m/e) shows considerable variation, partly because the hydrogen partial pressure was sensitive to

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Table 5

SUMMARY DATA OF BACKGROUND GASES AND GASES EVOLVED FROM LIQUID POLYMER BEFORE IRRADIATION

m/e	Probable Gas Species	LP-0 Background 1.2×10^{-5}	LP-0 Polymer 4×10^{-6}	LP-1 Background 3.9×10^{-6}	LP-1 Polymer 2.3×10^{-5}	LP-1 Polymer 7.3×10^{-5}	LP-1 Post-Test Background 3.2×10^{-5}	LP-2 Polymer 2.4×10^{-6}	LP-2 Post-Test Background 7.3×10^{-6}
2	H ⁺	4400	4800	950	2800	2400	Not taken	1770	613
12	C ⁺	16	12	13	28	10	17	16	13
13	CH ⁺	10	7	1	7	3	7	5	2
14	CH ₂ ⁺ , N ⁺	31	24	6.5	20	9	13	14	9
15	CH ₃ ⁺	113	78	11	52	27	40	42	14
16	CH ₄ ⁺ , O ⁺	112	73	22	54	26	40	42	24
17	OH ⁺ , CH ₅ ⁺	7	4	53	17	10	13	13	21
18	H ₂ O ⁺	12	11	186	48	31	40	35	63
25	C ₂ H ⁺	0.8	1.0	0.5	0.6	0.5	1.2	0.9	1.4
26	C ₂ H ₂ ⁺	3.6	4.6	2.3	3.3	2.6	7	4.6	8.1
27	C ₂ H ₃ ⁺	3.9	5.1	5.5	5.6	3.1	1.1	6.6	7
28	C ₂ H ₄ ⁺ , CO ⁺ , N ₂ ⁺	100	100	100	100	100	100	100	100
29	C ₂ H ₅ ⁺	2.2	3.0	2.7	3.1	2.9	6	3.0	3.5
30	C ₂ H ₆ ⁺	0.8	0.8	0.7	2.4	1.0	2.1	0.7	0.6
32	O ₂ ⁺	0.6	0.7	0.5	0.3	0.7	Neg.	0.3	0.2
36	C ₃ ⁺	Neg.	Neg.	1.3	Neg.	0.1	2.3	0.6	0.3
39	C ₃ H ₃ ⁺	0.4	0.4	1.3	1.0	Neg.	4.3	1.1	0.6
40	C ₂ O ⁺ , A ⁺	0.8	0.7	0.2	0.2	0.2	1.2	0.4	0.2
44	CO ₂ ⁺	1.6	2.2	14.6	3.3	2.7	11.4	0.8	9.6
45	?	1.6	2.1	Neg.	3.4	2.2	Neg.	1.4	Neg.
55	?	0.8	7.6	0.2	2.1	0.1	1.8	0.3	0.2
73	?	6.9	Neg.	Neg.	9.6	8.1	0.6	5.5	Neg.

the liquid nitrogen level on the polymer tubes and partly because a transfer calibration was required to obtain the relative peak heights. The mass spectrometer cannot scan the entire mass range from 2 to 300 AMU with one instrument setting. A magnet shunt is provided to scan the range of mass 2 to 40, and the range from mass 12 to 300 is scanned without the shunt. The relative peak height of mass 2 is obtained by equating the heights of masses 12 to 40 on the two scans.

Because of changes in gas composition in the interval between the taking of the two scans, an accurate value of mass peak 2 cannot be obtained. It is seen, however, that since composition is constantly changing, the peak heights for other gases are not absolute either.

The first set of scans, Test LP-0, shows a fairly constant level of hydrogen (2 m/e) and other atmospheric gases (H_2O^+ , 18 m/e, O_2^+ , 32 m/e, A^+ , 40 m/e, CO_2^+ , 44 m/e). A decrease in methane content (12, 15, and 16 m/e) is noted with the polymer present, although the intensity of peaks associated with higher hydrocarbons increased (25, 26, 27, and 29 m/e). The sporadic appearance of large peaks at 55 and 73 m/e was noted in subsequent tests. Their appearance cannot be explained at this time. The second set of scans, Test LP-1 shows a slight increase in the methane peaks (12, 15 and 16 m/e) and in the ethane peak (30 m/e) and a substantial hydrogen increase (2 m/e) when the polymer tubes were added. The third set of scans, Test LP-2

indicates a similar evolution of methane, although the lack of a pretest background scan gives less assurance of these data.

It is possible that residual hydrocarbon cleaning solvents, which were subsequently pumped away, were present when the first scan was taken, and obscured the detection of evolved hydrogen and methane from the polymer. Thus, it seems likely that a smaller amount of methane and a larger amount of hydrogen were present in the original polymer.

Table 6 shows the relative peak heights of gases taken during the first liquid polymer irradiation test, Test LP-1. It appears that there was a decrease in methane content (2, 14, 15, and 16 m/e) and an increase in carbon dioxide (44 m/e) during irradiation, with a subsequent increase in both methane and other atmospheric gases (12, 13, 17, 18, and 40 m/e) after irradiation. Presumably other conditions were the same, although liquid nitrogen level variations could possibly cause the anomalous results.

The results from the second liquid polymer irradiation, Test LP-2, are more significant. Summary data are shown in Table 7. Two polymer tubes were originally attached. One shattered when the tubes were cooled. The tube was sealed off, and the remaining tube was pumped down, recooled, and irradiated. This tube was removed after irradiation for electron spin resonance tests. Upon return, the tube was warmed, and the evolved gases were bled into the vacuum system through the variable leak. It is suspected that an air leak existed in

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Table 6

SUMMARY DATA OF TEST LP-1

Wt. %	Probable Gas Species	Warm Polymer before Test	Polymer under IN_2	Polymer under IN_2 & UV	Polymer under IN_2 after UV	Post-Test Background
		7.3×10^{-5}	1.0×10^{-6}	1.7×10^{-6}	8×10^{-7}	1.2×10^{-6}
2	H^+	2400	2250	620	Not taken	Not taken
12	C^+	10	7	10	26	17
13	CH^+	3	3	3	6	7
14	CH_2^+ , N^+	9	8	5	17	13
15	CH_3^+	27	26	11	51	47
16	CH_4^+ , O^+	26	26	16	53	40
17	C_2H^+ , CH_5^+	10	9	13	29	13
18	H_2C^+	31	28	36	90	40
25	C_2H^+	0.5	1.4	0.7	Neg.	1.2
26	C_2H_2^+	2.6	8.1	4.1	7.3	7
27	C_2H_3^+	3.1	9.6	7.1	9.2	1.1
28	C_2H_4^+ , CO^+ , N_2^+	100	100	100	100	100
29	C_2H_5^+	2.9	2.5	2.5	1.9	6
30	C_2H_6^+	1.0	1.6	2.5	0.7	2.1
32	O_2^+	0.7	Neg.	Neg.	Neg.	Neg.
36	C_3^+	0.1	0.6	0.7	Neg.	2.3
39	C_3H_3^+	Neg.	1.7	0.8	Neg.	4.3
40	C_2O^+ , A^+	0.2	0.5	0.3	2.6	1.2
44	CO_2^+	2.7	7.7	21.3	19	11.4
45	?	2.2	Neg.	0.3	3	Neg.
55	?	0.1	0.1	Neg.	Neg.	1.8
73	?	8.1	Neg.	0.3	3	0.6

Table 7

SUMMARY DATA OF TEST LP-2

Line	Probable Gas Species	Warm Polymer before test (2 tubes) 2.3×10^{-6}	Rewarmed Polymer before Test (1 tube) 2.3×10^{-6}	Polymer under LN ₂ 1×10^{-5}	Polymer under LN ₂ & UV 2.1×10^{-6}	LN ₂ low under UV 3.8×10^{-6}	Post-Test Backgrounds 8×10^{-7}	Gas from Polymer Tube Bled with Air Leak	
								Background 7.8×10^{-6}	Gas Admitted 7.3×10^{-6}
2	H ⁺	1770	955	540	600	2400	613	533	85
12	C ⁺	16	29	19	24	14	13	26	32
13	CH ⁺	5	21	2	2	6	2	3	2
14	CH ₂ ⁺ , N ⁺	14	42	5	6	14	9	16	108
15	CH ₃ ⁺	42	119	9	11	37	14	12	3
16	CH ₄ ⁺ , C ⁺	42	102	25	24	45	24	30	26
17	OH ⁺ , CH ₅ ⁺	13	3	29	23	8	21	42	4
18	H ₂ O ⁺	35	5	91	69	27	63	115	5
25	C ₂ H ⁺	0.9	2.0	-	-	2.2	1.4	0.4	0.2
26	C ₂ H ₂ ⁺	4.6	9.4	1.6	-	11.8	8.1	3.7	0.7
27	C ₂ H ₃ ⁺	6.6	10.7	2.3	2.7	12.4	6.9	4.4	1.4
28	C ₂ H ₄ ⁺ , CO ⁺ , N ₂ ⁺	100	100	100	100	100	100	100	100
29	C ₂ H ₅ ⁺	3.0	5.1	2.8	2.1	4.1	3.5	3.9	1.6
30	C ₂ H ₆ ⁺	0.7	1.4	0.7	0.5	0.7	0.6	1.5	0.2
32	C ₂ ⁺	0.3	0.3	-	-	-	0.2	3.7	3.4
36	C ₃ ⁺	0.6	0.4	-	-	-	0.3	-	-
39	C ₃ H ₃ ⁺	1.1	3.1	-	-	1.1	0.6	1.3	0.3
40	C ₂ O ⁺ , C ₄ ⁺	0.4	0.7	-	-	0.6	0.2	0.7	1.0
44	CO ₂ ⁺	0.8	1.9	10.4	10	3.3	9.6	4.3	1.1
45	?	1.4	2.2	-	-	2.0	-	-	-
55	?	-	0.9	-	-	2.3	0.2	-	-
73	?	5.5	6.2	-	-	2.3	-	-	-

the bleed system, and the results are questionable.

During the irradiation, a blown fuse disabled the automatic liquid nitrogen level control. Before this was detected and repaired, the level fell several centimeters below the usual operating level. A mass spectrometer scan was taken during this interval, and the results are also shown in Table 7. It is seen that when the first tube shattered and the second tube was warmed, the system content of methane and certain atmospheric gases increased. These were reduced to their original intensities when the tube was again cooled, and no increase was noted upon irradiation, except for carbon dioxide (44 m/e). However, when the liquid nitrogen level fell, considerable quantities of hydrogen, methane, and hydrocarbon ions with two carbons were released. The subsequent bleeding-in of the gases from the warmed tube showed increases only in atmospheric gases with no hydrocarbons present.

It is therefore concluded that hydrogen, methane, and carbon dioxide are dissolved in the liquid polymer in small quantities and that irradiation either facilitates their dissolution or generates additional quantities through bond breakage. However, the gases are not liberated from the polymer at liquid nitrogen temperatures, because of their reduced mobility in the frozen state.

6. Mass Spectrometry of the Solid Polymer

Test SP-1 was conducted with two fused silica tubes containing pieces of solid polymer. Upon initial pumping, the pressure

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fell to the 10^{-5} torr range, and large pressure fluctuations, from 6×10^{-5} to 5×10^{-4} torr, were observed for 30 min. After pumping overnight, the pressure fell to the 10^{-7} torr range and remained quite low throughout the test. Thus the solid polymer is more easily degassed than the liquid. Table 8 lists the significant data from Test SP-1. No significant methane evolution was observed. The hydrogen content of the system increased somewhat when the polymer tubes were attached, although no increase in intensity resulted from the irradiation. It appears, however, that the irradiation again liberated carbon dioxide (CO_2^+ , 44 m/e; C^+ , 12 m/e).

D. Future Work

These initial experiments have demonstrated several techniques and modifications that can markedly improve differential transmittance spectra, electron spin resonance spectra, and mass spectrometric analysis of the gases evolved from the polymers.

Differential transmittance spectra will be obtained on all materials photolyzed in the equipment shown in Figure 3. These spectra will be obtained directly by differential measurements. Experimentally, the contribution of the background residual gases can be reduced and stabilized by baking the vacuum system each time an experiment is conducted. In addition, greater stability can be obtained, at the expense of sensitivity, by incorporating a variable conductance between the polymer tubes and the mass

Table 8
SUMMARY DATA OF TEST SP-1

m/e	Probable Gas Species	Background 8×10^{-7}	Warm. Polymer before test 2.4×10^{-6}	Polymer under LN ₂ 7.5×10^{-7}	Polymer under LN ₂ & UV 8×10^{-7}	Polymer under LN ₂ & UV 5×10^{-7}	Warm. Polymer Gas Bleed 9.5×10^{-7}
2	H ⁺	613	1300	3400	1770	2050	1350
12	C ⁺	13	37	43	164	106	176
13	CH ⁺	2	10	22	15	11	32
14	CH ₂ ⁺ , N ⁺	9	21	51	34	31	36
15	CH ₃ ⁺	14	44	104	30	23	37
16	CH ₄ ⁺ , O ⁺	24	56	116	100	69	158
17	OH ⁺ , CH ₅ ⁺	21	28	12	27	22	5
18	H ₂ O ⁺	63	67	20	40	39	7
25	C ₂ H ⁺	1	2	4	2	1	7
26	C ₂ H ₂ ⁺	8	8	14	8	7	3
27	C ₂ H ₃ ⁺	7	11	16	8	7	3
28	C ₂ H ₄ ⁺ , CO ⁺ , N ₂ ⁺	100	100	100	100	100	100
29	C ₂ H ₅ ⁺	4	6	5	4	2	2
30	C ₂ H ₆ ⁺	1	2	2	1	1	1
32	O ₂ ⁺	0.2	0.3	0.4	Neg.	Neg.	Neg.
36	C ₃ ⁺	0.3	1.3	1.3	Neg.	Neg.	Neg.
39	C ₃ H ₃ ⁺	0.5	3.9	3.9	2	Neg.	Neg.
40	C ₂ O ⁺ , K ⁺	0.2	0.9	1.4	Neg.	Neg.	Neg.
44	CO ₂ ⁺	9.6	14	4.1	16	11	4
45	?	-	1	0.4	-	-	-
55	?	-	0.8	0.5	-	-	-
73	?	-	1.4	1.3	-	-	-

spectrometer and pumping system. This will permit all mass spectrometer traces to be taken at a constant pressure. Greater stability in the composition of gases in the vacuum system can be obtained by maintaining a constant liquid nitrogen level on the polymer tube Dewar.

However, the stabilized background will be of value only if improvements are made in the data analysis. These must take the form of an accurate calibration (fractionating spectra determination) for all background gases and suspected evolved gases. When this is accomplished, a computer program can be written to determine the intensities and identity of gas species present in the vacuum manifold.

An additional improvement that would facilitate the identification of hydrocarbon species is the modification of the mass spectrometer to permit variation of the ionizing potential in the tube. With this modification, "appearance potentials" could be determined for selected species.

APPENDIX A

SILICONE SYNTHESIS

I. SYNTHESIS OF LINEAR POLYDIMETHYLSILOXANE

A linear low-molecular-weight polymer was prepared by standard techniques but with the scrupulous avoidance of any aromatic contamination.

A. Octamethylcyclotetrasiloxane (ref. 13)

A 2-liter 3-neck flask was assembled with a thermometer, stirrer, condenser, and an adding funnel protected with a drying tube. By using a syringe, the plastic bag technique (ref. 14) was employed for transferring 400 ml of dichlorodimethylsilane (Union Carbide Corp.) in an atmosphere of prepurified nitrogen to the adding funnel. The silane was added as rapidly as dropwise addition would permit to 1200 ml of water, which had been previously charged into the flask. With the intermittent application of an ice bath, the temperature was maintained at 15 to 20°C throughout the vigorously stirred addition. The nonaqueous phase was extracted with 300 ml of diethyl ether, washed with water until neutral, and dried over sodium sulfate. After filtration, the solvent was removed on a rotating evaporator (Rinco), and the residue (~ 250 ml) was distilled rapidly through a 6 x 3/4-in. insulated Vigreux column. The fraction boiling at 164 to 171°C/745.5 mm was collected and weighed (123 g).

This fraction was then carefully redistilled by using the previously described apparatus. The fraction boiling at 170.0 to 173.0°C/738.7 mm was collected in two equal parts. Each of the two parts had an index of refraction, $n_D^{27.6}$, equal to 1.3932. This value is in essential agreement with that reported by Hunter (ref. 15), and the boiling point reported (ref. 13,16) is the same. A total of 81 g of the cyclic tetramer was obtained.

B. Linear Polydimethylsiloxane (by Catalytic Rearrangement ref. 13)

Into a 250-ml g.s. Pyrex bottle was charged 52 ml of the cyclic tetramer (octamethylcyclotetrasiloxane), 25 ml of diethyl ether, and 9.6 ml of concentrated sulfuric acid. The stopper was secured by wire and the bottle allowed to shake in a Eberbach shaking machine for 24 hr at ambient room temperature. After this time, the thick mass was diluted with 50 ml of diethyl ether, 25 ml of water was added, and the bottle was shaken for 1 hr. The solvent was separated and washed with three 10-ml portions of water. The still-acid solvent layer was diluted a little further with ether and dried over solid anhydrous potassium carbonate.

The filtrate was placed on a rotating evaporator to remove the solvent, and the residue was distilled through a long Claisen adaptor by using a Woods' metal heating bath. At still-pot temperatures up to 360°C, a few milliliters of liquid distilled at temperatures up to 117°C. The residue was allowed to cool in an atmosphere of prepurified nitrogen. The molecular weight

of the residue averaged 3,030 by Mechrolab vapor pressure osmometer determination.

Analysis (ref. 17). Found: H, 7.77, 8.09; C, 31.90, 31.84; Si, 34.59, 34.89. Calcd. for $(CH_3)_2SiO$: H, 8.16; C, 32.38; Si, 37.86.

The absorption spectrum of this polymer in isooctane was better than 98% transparent from 4,000 to less than 1900 Å, as shown in Figure 5. The $CH_3:Si$ ratio was close to the theoretical value of 2. At the pressures required for photolysis and at room temperature, about 10 to 15% of the polymer distilled over a 16-hr period.

C. Oxidative Cross-linked Dimethylpolysiloxane

A flask equipped with a two-way addition tube fitted with a gas-inlet tube and a reflux condenser was employed to cross-link a cyclic polysiloxane by the method of Hyde and Delong (ref. 18). The flask was charged with the cyclic polysiloxanes (pentamer and higher) obtained from the hydrolysis of dimethyldichlorosilane. This material was heated by means of a Woods metal bath to 220 to 230°C (pot temperature) for 16 hr while a slow current of air was continuously bubbled through the polymer. The resulting cross-linked material was of jello-like consistency and was water-white with an excellent ultraviolet transmission, 65% at 220 $m\mu$ and 40% at 200 $m\mu$.

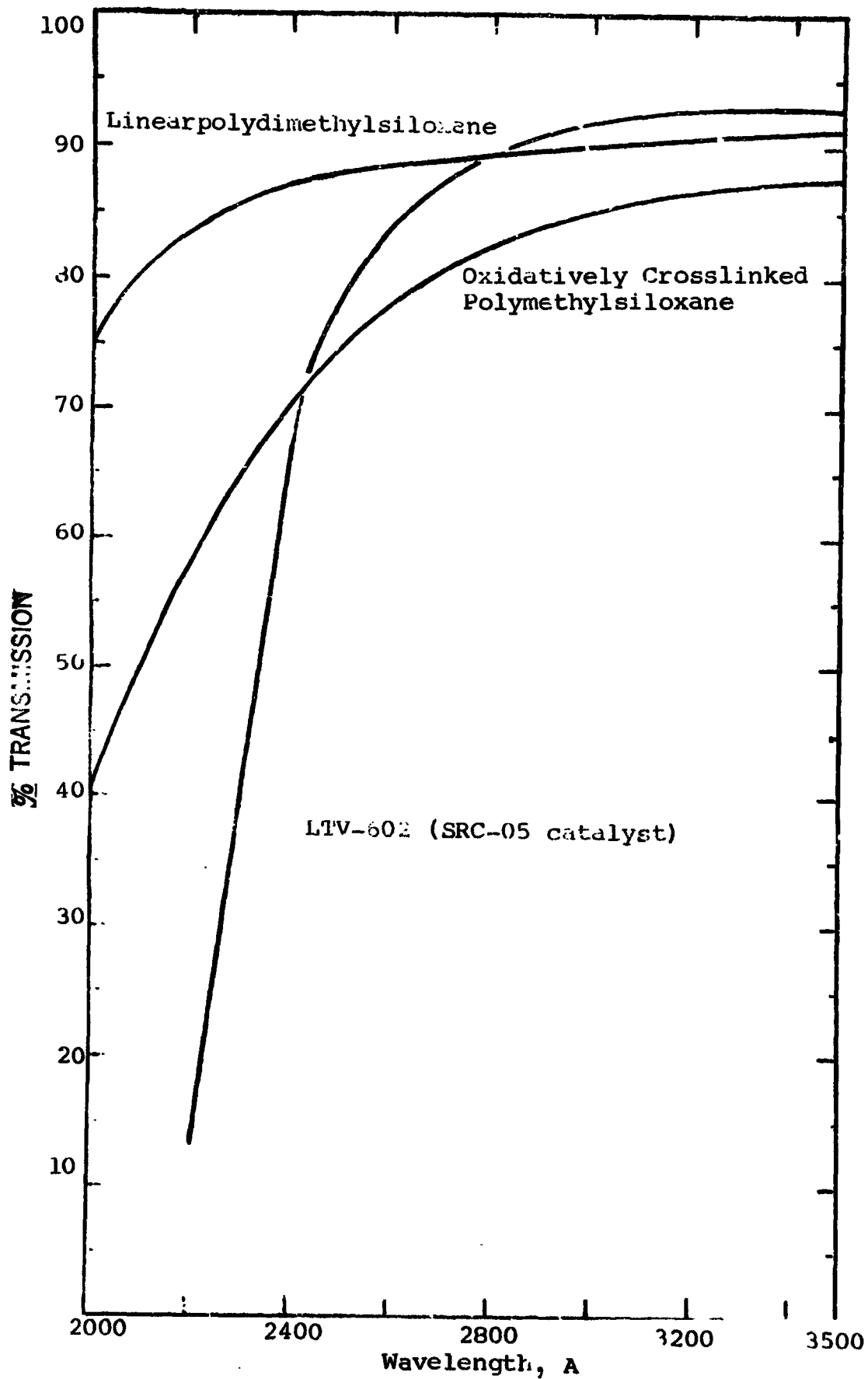


Figure 5
TRANSMITTANCE OF SILICONE POLYMERS
39

Analysis Calc. for $(CH_3)_2SiO$: C, 32.38; H, 8.16; Si 37.88,
Found (ref. 17) ² : C, 32.34; H, 8.06; Si, 33.51.

The transmission spectra of the oxidatively cross-linked polymer is also shown in Figure 5 and is compared with the linear polymer from which it was prepared and the linear RTV-602 obtained from the General Electric Company.

APPENDIX B

ELECTRON SPIN RESONANCE

Associated with every unpaired electron is a magnetic moment arising from an uncompensated spin. In a d.c. magnetic field the moments align in two sets, one parallel and one antiparallel to the applied field. Those electrons with spins parallel to the applied field have an energy $1/2 g\beta H$ less than those in a zero applied field, while those with spins antiparallel have an energy $1/2 g\beta H$ greater than the zero field value. The energy difference between the states is thus $g\beta H$, where H is the applied field, β is a constant, and g is characteristic of the system considered and is a measure of the contribution of the orbital moment and the spin moment to the total moment.

If a radiation of frequency ν is applied to the sample, some electrons in the lower energy state absorb energy from the radiation and jump to the upper state, providing

$$h\nu = g\beta H.$$

Any system in thermal equilibrium has more electrons in the ground state than in the higher state. In most cases, the distribution between the states follows a Maxwell-Boltzmann distribution, in which the ratio of the number in the higher state, n_1 , to that in the lower state, n_2 , is:

$$n_1/n_2 = \exp \left(-\frac{\Delta E}{k T} \right)$$

where ΔE is the separation between the two levels, k is the Boltzmann constant, and T is absolute temperature.

For the resonance absorption of radiation to continue there must be mechanisms that allow electrons in the upper state to lose energy and return to the lower state. Otherwise n_1 would approach n_2 , and no further absorption or radiation would occur. The relaxation process whereby the energy of the spins is shared with the thermal vibrations of the solid is known as spin-lattice interaction, with a strength measured by a spin lattice relaxation time. A long relaxation time is a consequence of a weak interaction and vice versa. With a long spin-lattice relaxation time, too high a power level may disturb the thermal equilibrium of the system and saturation of the resonance may occur. This saturation is manifested by an apparent decrease in the size of the absorption and usually by an increase in line width.

Any resonance spectrum has associated with it a number of important parameters:

- (1) The spectroscopic splitting factor, or g value
- (2) The value of any hyperfine splitting
- (3) The width of the absorption lines
- (4) The value of the splitting of the electronic levels

Therefore, the first three may be added when there is more than one unpaired electron present per atom or molecule.

The variations obtained in the g value arise through the admixture, via spin orbit coupling, of orbital moment to that of the spin. In nearly all free radicals the high asymmetry produced by the covalent bonds strongly quenches the orbital levels, leaving very little spin-orbit coupling. Consequently, the g values are found close to the free spin value of 2.0023, and thus this parameter is not too sensitive for distinguishing different spectra.

The hyperfine splitting of an electron spin resonance line arises from the interaction between the magnetic moment of the unpaired electron and the magnetic moments of the nuclei, which are embraced in the molecule orbits of the electron. The hyperfine interaction is divided into two sections, an anisotropic component and an isotropic component. The former arises from classical dipole-dipole interaction whereas the second is the quantum mechanically derived Fermi contact term.

In noncrystalline phases, the anisotropic part of the hyperfine splitting is smeared out by the random directions of the radical bonds with respect to the applied magnetic fields.

The isotropic contribution only is present for those orbitals that have a finite probability of wave function at the nucleus. For free atoms only 5 orbitals fulfill this condition, whereas for the molecular orbitals only the σ orbitals can produce

isotropic hyperfine splitting. Generally, the unpaired electron moves in a highly delocalized orbital, which may overlap with several nuclei possessing magnetic moments, each of which interact with the electron to produce a hyperfine splitting. For an unpaired electron equally coupled to n identical nuclei of spin I then, an absorption spectrum of $2nI + 1$ components is obtained. These components have a maximum intensity at the center and symmetrical distributions on either side, the ratio of intensities following the constants of a binomial expansion. Interactions with nuclei of different spins or interactions of different strengths with identical nuclear spins produce more complex spectra.

Parameters which influence line widths are:

- (1) Dipolar spin-spin interaction
- (2) Spin-lattice interaction
- (3) Exchange interaction

The dipolar interaction between the unpaired electron and surrounding nuclei has already been mentioned in connection with anisotropic hyperfine splitting. A further spin-spin interaction can occur between the electron spins themselves if the free radical concentration is high enough.

Spin-lattice interaction covers any process by which the electrons share energy with the molecule or lattice. Spins can exchange energy with the lattice vibration of the appropriate frequency or by scattering a quantum from the lattice and changing

its value. Generally in free radicals, because of the strong quenching of the orbital levels and the low spin-orbit coupling, this mechanism contributes but little to the broadening of the absorption lines.

Exchange interactions are a common feature of spectra whenever a high concentration of radicals is present. This exchange process can take place even when there is negligible chemical binding between molecules. The effect of exchange between similar ions or molecules is to narrow the line in the center and broaden it at the wings. Generally the change in shape of a line from a Gaussian to a Lorentzian shape is good evidence that exchange narrowing is present.

APPENDIX C

MASS SPECTROMETRIC ANALYTICAL METHODS

I. DISCUSSION

Raw mass spectrometric data consist of a series of charts of the relative quantity of various gas species in the manifold, segregated by the ratio of atomic weight (mass) to electric charge. The problems in identifying and quantifying particular gas species are related to the fact that several species may have the same mass-to-charge ratio (e.g., N_2^+ , CO^+ , and C_2H_4^+ all have an m/e of 28) and that a particular species (particularly hydrocarbons appear at several mass-to-charge ratios because of fractionation in the mass spectrometer tube (e.g., CH_4 appears at m/e of 2 (H_2^+), 12 (C^+), 13 (CH^+), 14 (CH_2^+), 15 (CH_3^+), 16 (CH_4^+) and possibly at higher m/e). A complete analysis of a mass spectrometer trace would involve identifying all species present and determining their fractionating spectra and the sensitivity of the mass spectrometer for each species. Simultaneous solution of the equations describing these data would provide the information desired.

Applying this to our situation, the following problems have been encountered. A background of residual gases is always present. It varies in content and quantity with pressure and previous exposure of the system to contaminant vapors. This background is usually several orders of magnitude larger than the signal we are looking for. The fractionating spectra for

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various gases have not been determined for our instrument. Many of the species present in our system are condensible at liquid nitrogen temperature, and the residual gas composition is quite sensitive to the liquid nitrogen level in the traps and particularly in the sample Dewar. These levels cannot be controlled adequately for the duration of a complete scan (usually about $\frac{1}{2}$ hour). Therefore, the composition changes between the start and finish of any scan. The gases evolved during an experiment contaminate the vacuum system and the mass spectrometer tube. This gives a different background before and after each experiment. Also, the contamination can decrease the sensitivity of the mass spectrometer markedly, which requires the use of different instrument settings for each trace. This may or may not change the fractionating spectra.

In the absence of fractionating spectra, only qualitative data can be inferred from the traces obtained to date. The mass spectrometer manufacturer has supplied some data, and others have been taken from the literature. However, these vary from instrument to instrument, thus reducing their applicability. A preliminary calibration for methane has been accomplished in our instrument. However, the background gases were not adequately controlled, and the data are not sufficiently precise to be used analytically.

The procedures used in identifying the evolving gases in these experiments are as follows. The peak heights for the various m/e ratios were taken from the charts and corrected for pressure variations during the scans. These were normalized to the 28 m/e peak to provide a means of direct comparison. They could have been normalized to some other peak or adjusted to equivalent total pressure, although these techniques gave somewhat more confusing results. Particular peaks (m/e ratios) were selected that are characteristic of certain gases. These were usually the parent peak (18 for water = H_2O^+), although sometimes a subordinate peak is more meaningful if the parent peak corresponds to more than one species (16 can be O^+ or CH_4^+ ; 15 is usually only CH_3^+ and is a better indicator for methane). Thus, by comparing "before", "during" and "after" traces, an indication of the evolving gases can be obtained.

II. METHANE CALIBRATION

A preliminary calibration (determination of the fractionating spectra) of methane was conducted in an ion-pumped system in which the background pressure was approximately 10^{-8} torr. The results are not directly applicable and are presented here to give an indication of the experimental errors and analytical problems inherent in this study. They also indicate the extent of the calibration necessary for quantitative analysis of the polymer scans.

The calibration was accomplished by admitting electronic-grade methane from a lecture bottle into the system through a variable leak. The pressure was stabilized at various levels, and mass spectrometer scans were taken. Table 9 lists the normalized significant peak heights at the various pressures, along with fractionating spectra from the literature. The data of Franklin et al (ref. 19) show that recombination of methane fragments can take place at higher pressures (10^{-3} torr) to produce peaks associated with hydrocarbons having two carbon atoms.

The experimental data show a fairly constant 12 peak; i.e., the ratio of intensities between 28 m/e and 12 m/e is fairly constant at all pressures. However, the 12 peak results not only from the carbon in methane, but also from the residual carbon dioxide and other hydrocarbons in the system. The fact that the experimental 15 and 16 m/e peak intensities do not fall in line with the values from the literature results from this background contribution to the 12 m/e peak and from the O^+ contribution to the 16 peak. The increase in 15 and 16 m/e peak intensities with increasing pressure indicates that our normalization to 28 m/e was not entirely appropriate for this display. The increase in pressure from 1.4×10^{-8} to 6×10^{-6} torr with pure methane should have reduced the background residual gases to a negligible level. There is, however, an indication that the pressure of the background gases also

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Table 9

SUMMARY OF METHANE CALIBRATION DATA

M/e	Background (No Methane) 1.4 x 10 ⁻⁸	METHANE ADMITTED TO:						Data Supplied With Instrument	Data from Ref. 19
		4.5 x 10 ⁻⁸	1.7 x 10 ⁻⁷	6.5 x 10 ⁻⁷	1.5 x 10 ⁻⁶	4.0 x 10 ⁻⁶	6.0 x 10 ⁻⁶		
12	24	35.6	24.6	20.4	27.2	14	43	24	24
13	7.8	16	26	27.4	30.6	21.4	74.5	50.5	68
14	22	34	54	52	61.7	44.5	150	110	162
15	39	92	163	204	239	271	c	820	1530
16	44	104	196	226	272	313	c	920	1785
17	58.5	a	a	9.7	10.5	7.2	6.3	-	81
18	166	a	a	18.7	13.4	6.9	4.9	-	-
24	a	a	0.4	0.4	0.4	0.4	6.5	-	-
25	a	2.4	1.9	1.4	1.5	1.7	1.8	-	-
26	20	16	11	7.7	7.8	9.0	9.6	-	2.6
27	38	29.2	14.5	8.3	8.3	7.0	7.5	-	7.6
28	100	100	100	100	100	100	100	-	7.4
29	16.6	12.4	6.2	5.0	3.2	3.1	2.5	-	40
32	b	b	a	0.1	0.2	b	a	-	-

a Data not taken

b Negligible peak height

c Off scale

increased, probably from contaminants in the methane admission system.

This analysis, then, indicates the extent to which the background residual gas environment influences the spectra and the precautions that must be taken in determining fractionating spectra.

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